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## Performance of lightweight cement pastes under CO<sub>2</sub> storage conditions

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### Abstract

The deployment of CO<sub>2</sub> underground storage is advancing fast, and the technology previously used to inject and extract different fluids to or from the formations should be evaluated considering the presence of this fluid in a supercritical state. For underground CO<sub>2</sub> storage, injection wells are cemented to isolate formations and protect the casing, using cement paste to fill the annular space between the casing and the borehole. Before hardening, the paste exerts pressure on the formations proportional to its specific weight, which cannot be higher than the formation's fracture gradient nor lower than its pore pressure. Therefore, the weight of the cementing pastes must be constantly controlled. As a solution for lowering pastes' density without compromising their mechanical properties, the addition of hollow glass microspheres (HGMS) has been considered. These consist of low-density micrometric hollow spheres with high crush strength. HGMS have been widely used for cementing underground wells. Nevertheless, the durability of the cement paste admixed with hollow glass microspheres has not been studied under a supercritical CO<sub>2</sub> saturated atmosphere. The cement sheath must grant isolation of the formation throughout the CO<sub>2</sub> storage project; therefore, its durability should be granted.

In this work, we intend to study the performance of cement pastes lightened with HGMS to determine whether their properties would be affected when in contact with supercritical CO<sub>2</sub>. For this purpose, it is important to assess the interaction between HGMS and cement paste to determine its initial properties. In previous research, the chemical and mechanical interactions between these two materials were already studied, confirming their compatibility and the development of a chemical reaction between the HGMS and the cement paste. Consequently, HGMS modified the composition of cement paste, particularly the amount of calcium hydroxide and calcium silicate hydrate. In addition, in the presence of supercritical CO<sub>2</sub>, the cement paste undergoes specific changes in its chemical composition, which are also related to the dissolution of calcium hydroxide and calcium silicate hydrate. Research has already been carried out to understand the implications of this exposure, verifying the effect on the physicochemical properties of cement pastes. As carbonation progresses, variations in the physical and chemical properties of the cement can be seen.

Nevertheless, the interaction between a cement paste lightened with HGMS and supercritical CO<sub>2</sub> has not been evaluated yet. To this end, cement pastes with and without HGMS were subjected to a carbon dioxide-saturated atmosphere under 20 MPa and 90°C for 60 days. The pastes' chemical composition and compressive strength were measured before and after the carbonation. Furthermore, the carbonation front was visually determined using microscopy images.

It was determined that adding HGMS to the cement pastes affects the carbonation mechanisms of cement pastes. The presence of HGMS noticeably modified both chemical and mechanical properties of cement pastes under a supercritical CO<sub>2</sub> atmosphere, even the advancement of the carbonation front was modified by its addition. These observations could be related to the chemical interaction between HGMS and cement paste, which, in the presence of supercritical CO<sub>2</sub>, eases the advancement of the carbonation front and the induced effects on pastes' properties given the unconnected porous structure provided by the hollow spheres. Therefore, special attention should be paid when cementing CO<sub>2</sub> injection wells with lightened admixtures that can react with cement hydration products.

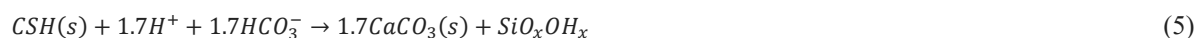
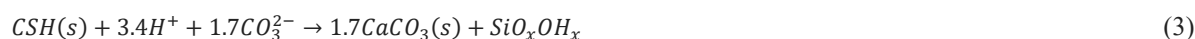
*Keywords:* cement paste; hollow glass microspheres; carbon dioxide geological storage

## 1. Introduction

In the past decades, since the industrial revolution, the greenhouse gas (GHG) concentration in the atmosphere has notably increased because of human activities [1]. Among all the emitted GHG, the most abundant one is CO<sub>2</sub>, which presents its highest concentration in the atmosphere in thousands of years [2]. The average global warming is about 1.0°C since the pre-industrial era. Given the high amount of energy production and other human activities, it is highly likely that by 2050 this value will reach 1.5°C [3]. Therefore, some short and midterm solutions should be applied to improve the current situation, for which carbon capture and storage (CCS) arises as one of the main possible solutions since it could reduce GHG emissions by almost 90% [2], [4].

By applying CCS, CO<sub>2</sub> could be stored in deep underground reservoirs after being extracted from punctual sources, i.e., power plants, and industries, among others. To achieve CO<sub>2</sub> storage, it should be injected through injection wells. These consist of a deep well composed of an interior casing/metallic pipeline surrounded by a cement paste and the rock mass. The integrity of the wellbore system while being exposed to CO<sub>2</sub> deep injection wells conditions must be assured. For this purpose, among all the parts composing these wells, this research focuses on the cement sheath, which should grant the well stability, contain the casing and act as a seal to avoid fluid migration [5].

Under these conditions, the hydrated cement paste will undergo changes in its chemical composition related to variations in its microstructure, porosity and mechanical behaviour. The chemical interaction between cement hydration products (mainly portlandite – CH – and calcium silicate hydrate – CSH) is that expressed in reactions 1 to 7 [6 - 11], where firstly the CO<sub>2</sub> dissociation occurs (Reaction 1) followed by the CH and CSH carbonation (Reactions 2 to 5). Both CH and CSH are present in solid state (s) and their carbonation gives as result solid calcium carbonate (CaCO<sub>3</sub> (s)).



Cement sheath degradation in terms of carbonation of cement hydration products is paramount. It should be appropriately assessed since fluid migration must be guaranteed to ensure the sealing is functional. This research focuses on studying lightened cement paste used for well cementing. The cement is lightened with hollow glass microspheres (HGMS) to obtain a lightweight cement paste, which is useful for injection wells in low-strength rock formations [12]. HGMS are widely used for oil well cementing with the ability to reduce the specific weight of the cement paste without severely affecting its hardened properties [12]. In previous research, the chemical interaction between HGMS and cement hydration product was already proven [13]. However, there is not much research regarding the influence of HGMS on the durability of lightweight cement paste subjected to CO<sub>2</sub> injection wells. This research aims at analysing the performance of lightened cement pastes under these conditions by comparing the changes occurring in plain and lightened cement pastes after being subjected to supercritical carbonation. From the studied samples, preliminary results on chemical changes by means of X-Ray diffraction (XRD) were measured and

related to the variation in the mechanical performance as measured by uniaxial compressive strength (UCS) tests.

## 2. Materials and methods

The materials used in this study were Class G portland cement, HGMS (3M), deionized water and polycarbonate-based superplasticizer. The cement, provided by Petroquímica Comodoro Rivadavia (Argentina), has a density of  $3.18 \text{ g/cm}^3$  [14]. The superplasticizer was ADVA 570 from GCP Applied Technologies. Two types of HGMS were used: HGMS27 and HGMS41. HGMS27 have a density of  $0.28 \text{ g/cm}^3$ , a mean particle size ( $D_{50}$ ) of  $30 \text{ }\mu\text{m}$  and a crushing strength of  $27 \text{ MPa}$ . HGMS 41 have a density of  $0.46 \text{ g/cm}^3$ ,  $D_{50}$  of  $40 \text{ }\mu\text{m}$  and a crushing strength of  $41 \text{ MPa}$ .

Table 1 shows the oxide composition of class G Portland cement, HGMS27 and HGMS41.

For the dosing of the pastes, a water-to-solid ratio (w/s) of 0.44 was used following the specifications given by the American Petroleum Institute for the design of class G oil well cement pastes [14]. HGMS27 and HGMS41 were added as 10% by weight of cement replacement. Table 2 shows the names and proportions of the pastes used in this research.

Table 1: Oxide composition for class G Portland cement, HGMS27 and HGMS41.

Compound	Class G Portland cement	HGMS27	HGMS41
SiO <sub>2</sub>	19.30	60.30	60.90
CaO	52.20	11.40	11.00
Na <sub>2</sub> O	0.53	6.37	5.98
Al <sub>2</sub> O <sub>3</sub>	3.30	0.08	0.14
MgO	3.27	0.08	0.10
Fe <sub>2</sub> O <sub>3</sub>	18.20	0.04	0.05
Br <sub>2</sub> O	1.74	0.84	0.90
P <sub>2</sub> O <sub>5</sub>	0.14	0.57	0.56
SO <sub>3</sub>	2.09	0.27	0.29

Table 2: Cement pastes classification and dosages.

Paste	Cement (kg/m <sup>3</sup> )	HGMS27 (kg/m <sup>3</sup> )	HGMS41 (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	Superplasticizer (kg/m <sup>3</sup> )
CS00	1320.2	-	-	580.9	-
CS27	829.0	92.1	-	405.3	2.8
CS41	952.5	-	105.8	465.6	2.1

Supercritical CO<sub>2</sub> (scCO<sub>2</sub>) is injected into deep geological reservoirs accessible through injection wells for storage. The cement paste occupying the annular space between the formation and the casing will undergo specific chemical interactions called carbonation. Carbonation is a chemical process in which the scCO<sub>2</sub> combined with the aqueous phase in the reservoir reacts with the alkaline components of cement, i.e., portlandite (CH) and calcium silicate hydrate (CSH), as is shown in reactions (2) to (4). CH is consumed first, decreasing pH and allowing the advancement of the scCO<sub>2</sub> into the cement matrix. The chemical composition changes progressively affect the pastes' microstructure [15].

The cement samples were subjected to high pressure (20MPa) and temperature (90°C) conditions similar to the geological storage of scCO<sub>2</sub> with a specially designed cell shown in Fig. 1. The samples were in a CO<sub>2</sub>-saturated atmosphere with water maintained for 60 days. Hereafter, the carbonated cement samples from Table 2 have been identified as CS00C60, CS27C60 and CS41C60, where C60 stands for "carbonated for 60 days".



Fig. 1: Cell used for subjecting cement samples to CCS conditions

Given the close relationship between the changes in the cement's pore structure and the modification of its chemical composition, the latter will be measured for each cement paste before and after carbonation. For this purpose, X-Ray diffraction tests (XRD) with Rietveld quantifications were performed on powder samples of the three cement pastes before and after 60 days of carbonation.

This test mainly relies on the Bragg law, after which it is possible to establish a relationship between the diffraction degree of the X-rays and the distance between each plane of the crystals present on the sample. This is defined in Equation 6, where  $d$  is the interplanar distance,  $\theta$  is the refraction angle,  $\lambda$  is the wavelength and  $n$  is an integer.

$$2 \cdot d \cdot \sin(\theta) = n \cdot \lambda \quad (6)$$

Each crystalline phase corresponds to a different diffraction angle. If the sample tested is a monocrystal, the result of this test is easily analyzed since only one  $\theta$  will be obtained. Hydrated cement pastes present many crystalline phases (portlandite, calcite, aragonite, brownmillerite, among others) and an amorphous phase (mainly calcium silicate hydrate). Therefore, the analysis of this kind of material presents some additional complexity.

Given that there exists previous research in which XRD patterns were obtained for cement pastes [16], [17], the characteristic peaks of the diffractogram of this material are well known. With this information, it is possible to apply the Rietveld method to quantify the amount of each crystalline phase of interest for this research. This method is based on a minimum square refinement until obtaining the best adjustment of the diffractogram for the tested powder and then integrating the intensity associated to each diffraction angle  $\theta$ .

Finally, uniaxial compressive strength tests were performed to assess the relationship between the mechanical properties, the presence of HGMS of different classes and the effect of carbonation. It consists of subjecting cylindrical specimens of 1.5 inches diameter and 3 inches height to compressive stress until failure is reached. This test was performed on three samples for each dosage to obtain their uniaxial compressive strength before and after carbonation.

### 3. Results and Discussion

The carbonation process advances through the cement samples from its outer part until reaching its core. Fig. 2 schematically shows a cut of a cylindrical sample subjected to supercritical carbonation. The color schematizes a pH indicator that turns purple for a pH higher than 9. Given the carbonation process, the CH, which is the phase that increases the cement's pH, transforms into  $\text{CaCO}_3$  decreasing the material's pH from approximately 12 to less than 9 from the outer part of the sample to the core. For quantifying the influence of supercritical carbonation in cement's

mechanical behaviour, XRD patterns for the core of the sample were obtained.

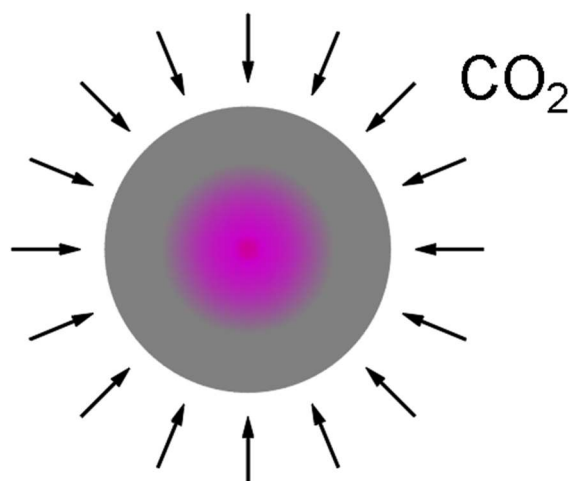


Fig. 2: Sketch of the cross section of a partially carbonated cement sample coloured with pH indicator

Fig. 3 shows the CH content in cement pastes before and after carbonation. The results show that cement pastes lightened with HGMS (CS27 and CS41) present lower amounts of CH before carbonation than CS00. This is due firstly to the less cement these dosages have. Considering the masses indicated in Table 2 and the densities of class G cement, HGMS27 and HGMS41, the dosages in volume could be obtained (Table 3). The cement volume contents for CS27 and CS41 is lower than that of CS00 due to the addition of HGMS27 and HGMS41, respectively. Even though they only replaced 10% by weight of cement, since their density is considerably low, the volume they occupy in the pastes is high. Moreover, both HGMS present chemical interaction with cement hydration products called pozzolanic reaction. In this chemical reaction CH consumes HGMS's outer shell to form CSH resulting in a lower initial amount of CH in the cement paste [13].

Table 3: Cement pastes dosages by volume.

Paste	Cement [m <sup>3</sup> /m <sup>3</sup> ]	HGMS27 [m <sup>3</sup> /m <sup>3</sup> ]	HGMS41 [m <sup>3</sup> /m <sup>3</sup> ]	Water [m <sup>3</sup> /m <sup>3</sup> ]	Superplasticizer [m <sup>3</sup> /m <sup>3</sup> ]
CS00	0.42	-	-	0.58	-
CS27	0.26	0.33	-	0.41	0.003
CS41	0.30	-	0.23	0.47	0.002

In addition, there are some expected variations in the chemical composition due to the carbonation process, which first dissolves CH and then forms some polymorphs of calcium carbonate, mainly calcite and aragonite. Thus, the advancement of the carbonation can be measured in terms of CH, calcite and aragonite content obtained from XRD tests. Fig. 3 shows the CH content of the core of each cement paste before and after carbonation (C00 and C60, respectively). There is no significant difference in CH content between carbonated and non-carbonated CS00 samples (plain cement). This means that the core of plain cement (CS00) samples was not affected by the supercritical carbonation performed in this research. The carbonation front did not reach the most inner part of CS00 samples. However, portlandite (CH) dissolves completely due to scCO<sub>2</sub> penetration in samples CS27 and CS41. This means that the penetration of scCO<sub>2</sub> was deeper for the lightened cement pastes.

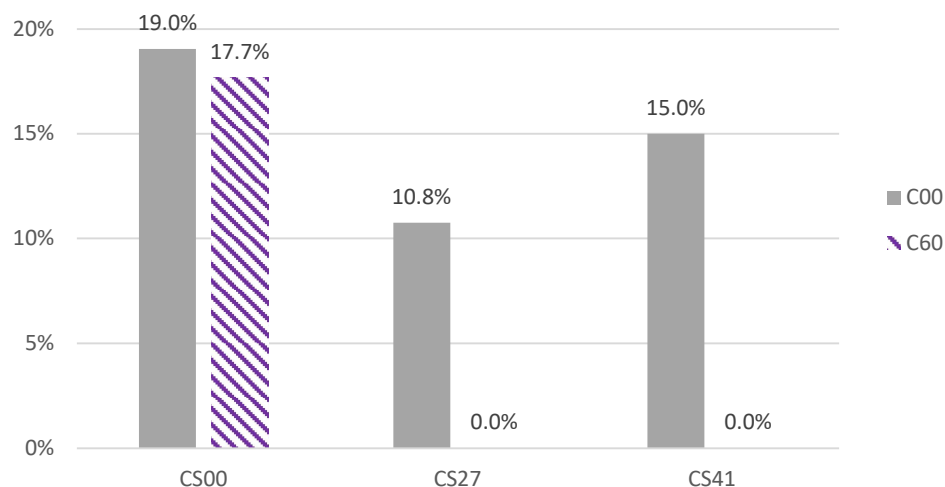


Fig. 3: Portlandite content for the core of the cement samples before (grey) and after (purple) carbonation (C00 and C60, respectively) for plain cement (CS00) and cement pastes modified with HGMS (CS27 and CS41).

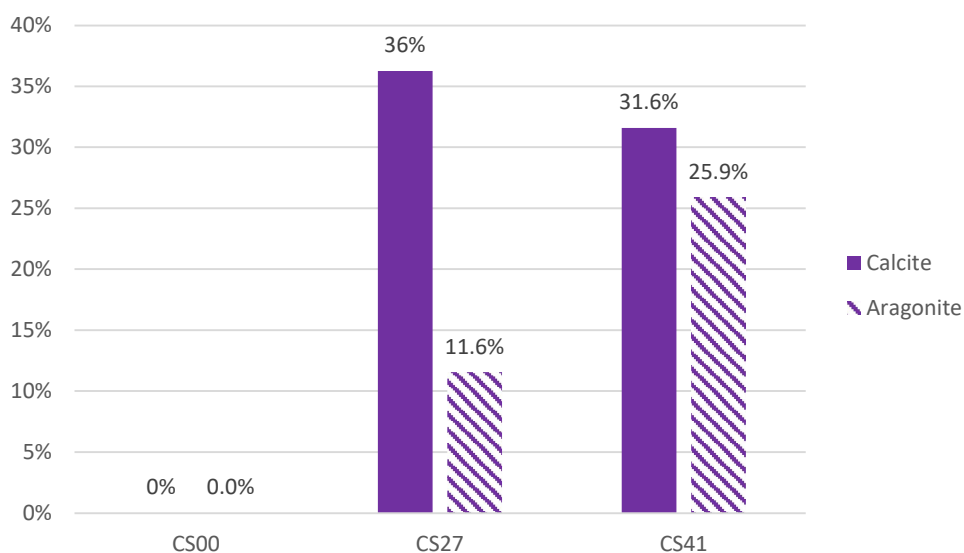


Fig. 4: Change in content of calcite and aragonite after carbonation (measurement at the core of the cement samples).

Fig. 4 shows the increase in the absolute contents of the two main crystalline calcium carbonate phases in these samples, calcite and aragonite. It is noteworthy that CS00 presents no increase in any of them, which further shows that supercritical carbonation did not affect the core of the CS00 sample.

For lightened cement pastes (CS27, CS41), even though they contain around 10% and 15% of portlandite, the amount of calcite reaches between 30% and 40% while the aragonite content is around 10% for CS27 and 25% for CS41. Given these high values of both calcium carbonate crystalline phases, it could be argued that not only the portlandite has been dissolved in the core of CS27 and CS41 samples, but also some of its CSH.

The amount of each polymorph could also imply a more important advance of  $\text{scCO}_2$  in the cement samples. To further understand the implications of having calcite or aragonite crystals within the sample's core after carbonation,

the conditions under which each of these is created should be considered. In this regard, Morandea et al. [9] studied the mechanisms of CH and CSH carbonation. Among other conclusions, they found a relationship between the formation of less stable calcium carbonate polymorphs (i.e., aragonite and vaterite) and the actual composition of CSH. The lower the Ca/Si ratio of CSH, the more decalcified the CSH, and the higher the amount of aragonite and vaterite formed in the carbonation process. CS27 and CS41 have the presence of HGMS, which present the pozzolanic activity from which low Ca/Si CSH is obtained [13]. Thus, an increase in the aragonite phase is expected in these cement pastes.

The temperature and the pH also affect the formation of different calcium carbonate crystals. According to Chang et al. [18], aragonite results a thermodynamically stable polymorph for temperatures above 60°C. However, any metastable aragonite will transform into calcite after exposure to temperatures from 60°C to 80°C for 1000 to 1300 minutes. Given the supercritical carbonation performed in this research, the formed aragonite should be stable and shall not evolve into calcite. Nevertheless, if some metastable crystalline polymorphs of calcium carbonate exist after this carbonation, it might have transformed to calcite.

Finally, Chang et al. [18] argue that calcite generally results from the carbonation reaction in elevated pH environments of 11 or higher, while aragonite forms at lower pH, between 9 and 11. It should be considered that the non-carbonated cement matrix has a pH higher than 11.5, and the carbonated cement has a pH between 7 and 8 [17]. Furthermore, in previous research it was found that CS27C60 has more interconnected porosity than CS41C60 Martín et al. [13] and the carbonation front advance quicker in CS27 than in CS41. This could favour the formation of calcite in CS27 since it is being formed when the pH is still high.

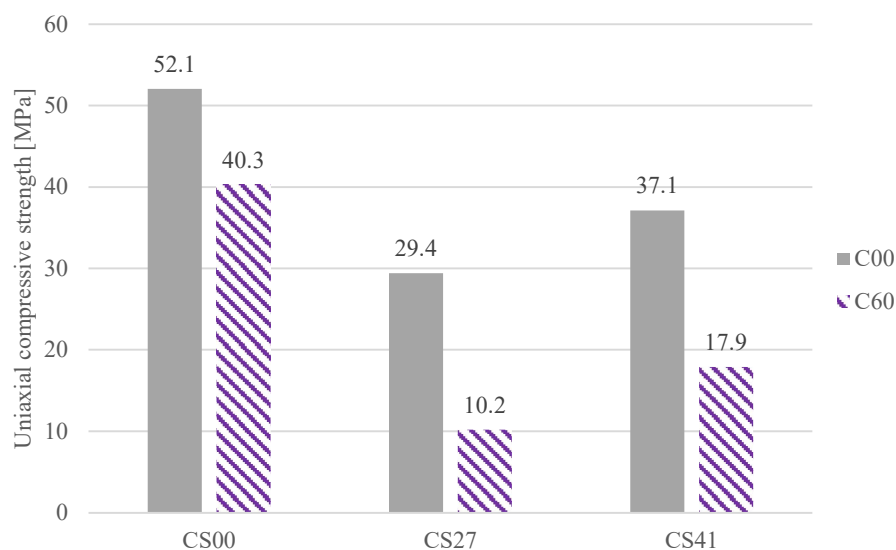


Fig. 5: Uniaxial compressive strength results

Since the main variation in the chemical composition of the cement matrix was already discussed, Fig. 5 shows the influence of the supercritical carbonation on plain and lightened cement samples' mechanical behaviour. As aforementioned, the modification of the cement matrix due to the carbonation is associated with changes in the microstructure [15] which, as shown in Fig. 5, influences the mechanical properties. After the supercritical carbonation, all cement samples yield a decrease in the uniaxial compressive strength. The absolute decrease for each cement paste is 12 MPa for CS00 and 19 MPa for CS27 and CS41. Nonetheless, it is more interesting to analyse these results as a fraction of the initial compressive strength, which yields a 23% decrease for CS00, 65% for CS27 and 52% for CS41.

CS27 results in the most affected cement paste in terms of UCS, followed by CS41 and CS00. The UCS of the cement samples relies on many parameters. CS27 is the cement paste modified with the lightest, most reactive with cement and less resistant HGMS, which means that the lowest values of UCS before and after carbonation should be expected.

These differences between HGMS27 and HGMS41 could be analysed from two points of view. On the one hand, since there is more volume of HGMS27 than HGMS41 and the former is more reactive than the latter, there will be considerably more consumption of portlandite due to the pozzolanic reaction. Although it could be argued that the CSH resulting from this chemical reaction is denser than the portlandite initially present on the cement matrix, a report made by the International Union of Laboratories and Experts in Construction Materials, Systems and Structures (RILEM) states that the higher consumption of portlandite and the associated decrease in pH favours the carbonation penetration [19]. On the other hand, the higher reactivity of HGMS27 than HGMS41 implies that the pozzolanic reaction will consume more of their outer shell. Thus, the final strength of HGMS27 might be even lower than 27 MPa. Since the cement samples were subjected to 20 MPa pressure and 90°C for achieving real CO<sub>2</sub> storage wells conditions, these microspheres probably broke throughout the supercritical carbonation process. Therefore, the porosity initially considered non-interconnected given to the cement matrix would turn out to be connected, favouring the advance of scCO<sub>2</sub> through the matrix [20].

By comparing results of XRD and UCS it can be noticed that, as shown in Fig. 3, Fig. 4 and Fig. 5, dissolution of CH and calcite and aragonite crystals formation occurred while there is a decrease in the UCS due to the supercritical carbonation. These results appear to be related to deeper carbonation of CS27 and CS41 samples, which results in a higher decrease in the UCS of these pastes, higher consumption of CH and more formation of calcium carbonate polymorphs. A relationship between the changes in the calcite formation and the UCS can be appreciated. However, as aforementioned and confirmed by previous research [13] the UCS relies on many parameters other than the depth of cement carbonation. Carbonation and the crystalline phases appearing after it depends on many conditions, i.e., cement composition, chemical interaction between HGMS and cement paste, HGMS capacity to withstand supercritical carbonation conditions, among others. Hence, finding a direct relationship between XRD results and mechanical behaviour is still challenging. These preliminary results further analyse the interaction between HGMS of different classes, cement hydration products and CO<sub>2</sub>. However, further research is required to fully comprehend this complex behaviour.

#### 4. Conclusions

In this research we present preliminary results on the influence of lightened cement pastes with HGMS for CO<sub>2</sub> geological storage injection wells. The relationship between chemical composition obtained from XRD tests and uniaxial compressive strength were analysed for plain and lightened cement pastes with HGMS after supercritical carbonation for 60 days.

Adding HGMS in cement pastes affects the performance of the cement under these conditions, as shown by all the parameters studied in this research. To begin with, the portlandite consumption in the core of the samples was complete for cement pastes CS27 and CS41, while almost no change in the portlandite content was measured in CS00. Also, both CS27 and CS41 showed a high increase in the amount of calcium carbonate as two of its possible polymorphs, aragonite, and calcite. Moreover, the uniaxial compressive strength results show that for all the cement pastes, the compressive strength is degraded after the supercritical carbonation process. Regarding the fraction of the initial strength, the most affected cement paste is CS27.

A relationship between XRD and UCS results can be found when comparing lightened (CS27, CS41) and plain (CS00) cement pastes. CS00 core sample presents almost no variation in its chemical composition in contrast to CS27 and CS41, and the decrease in the UCS results is the lowest (23% against 65% and 52%). There exist many properties of the cement pastes that influence the mechanical behaviour, particularly the unconfined compressive strength. Among them we can find microstructure/porosity, chemical interaction between HGMS and cement, chemical changes due to cement carbonation and HGMS's mechanical properties. More research is being performed to fully understand the interaction of HGMS with cement hydration products under supercritical carbonation.

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# Performance of lightweight cement pastes under CO<sub>2</sub> storage conditions

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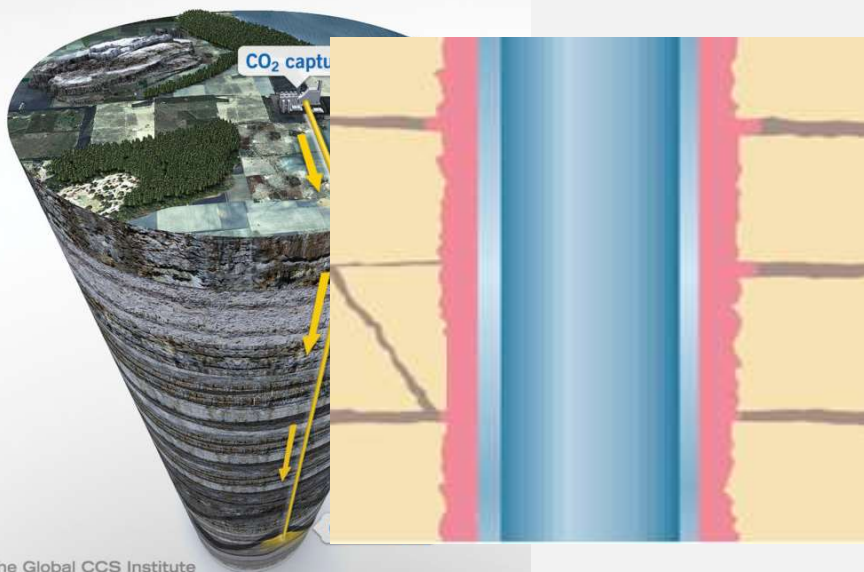
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DISCO<sub>2</sub>  
STORE

# Motivation and objectives

## CO<sub>2</sub> geological storage

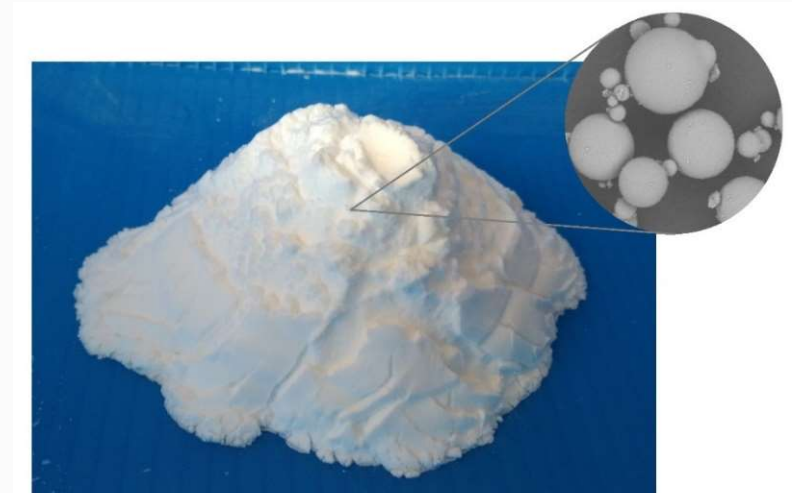
Chemo-mechanical behavior of  
lightweight cement pastes in CCS  
conditions



Provided by the Global CCS Institute

## Lightweight cement pastes

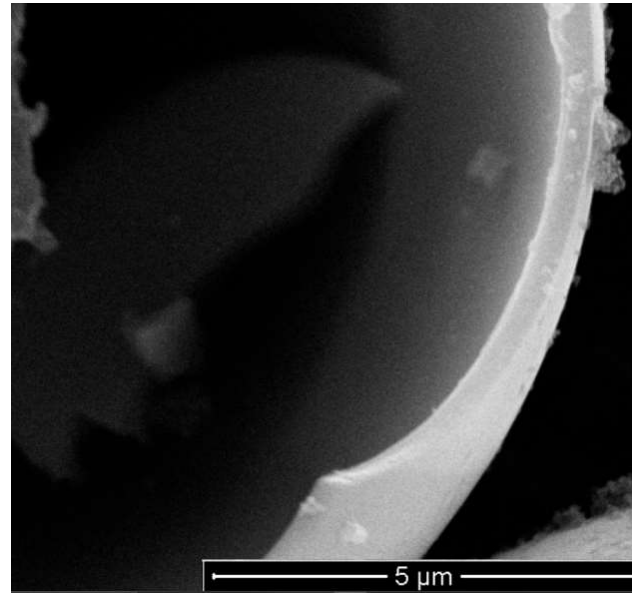
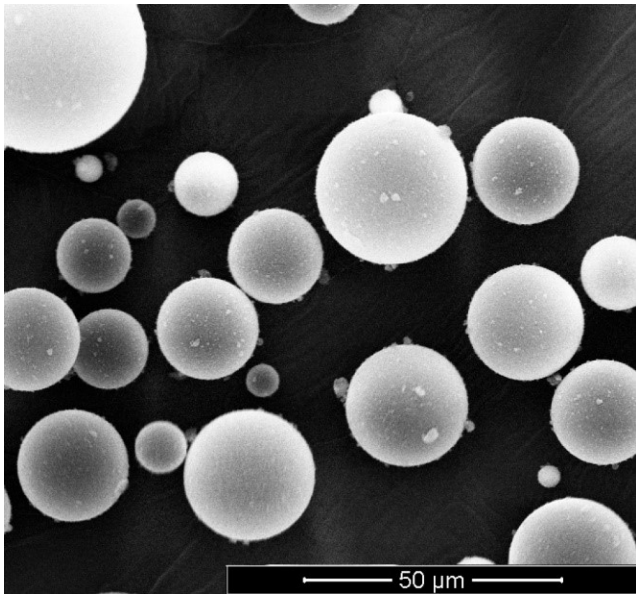
Chemical and mechanical influence of  
hollow glass microspheres (HGMS)  
in cement pastes



# Lightweight cement pastes

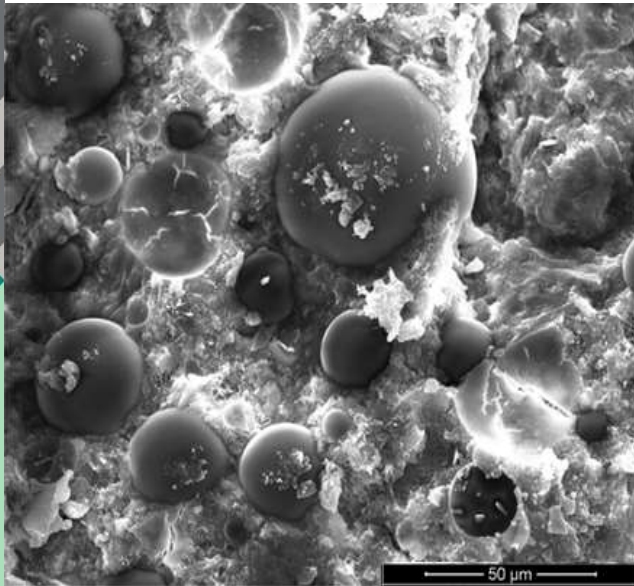


## HGMS

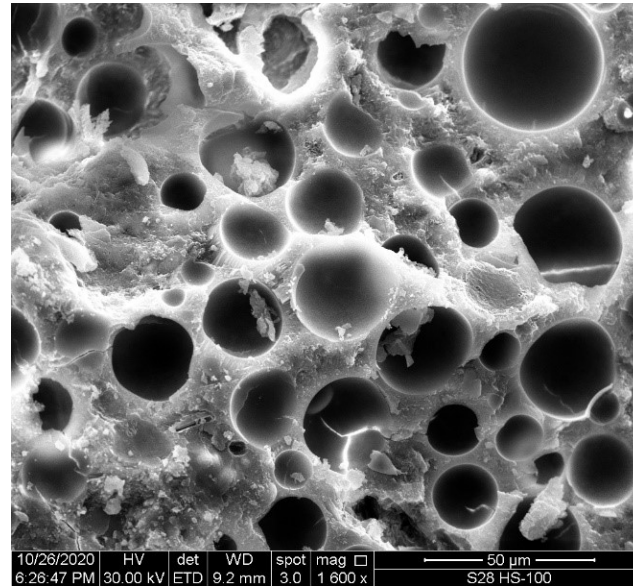


Compound	HGMS27	HGMS41
SiO <sub>2</sub>	60,3	60,9
CaO	11,4	11,0
Na <sub>2</sub> O	6,4	6,0

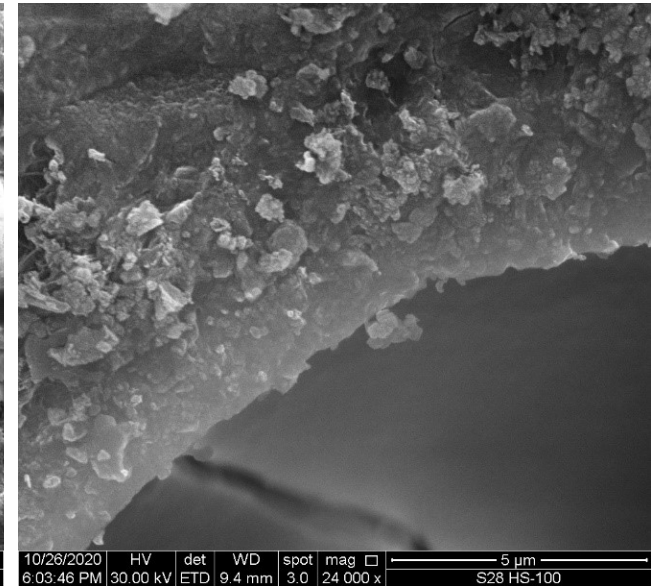
# HGMS with cement



28 days



100 days



Interphase  
100 days

## Cement pastes classification and dosages

Pastes	Cement [kg/m <sup>3</sup> ]	HGMS27 [kg/m <sup>3</sup> ]	HGMS41 [kg/m <sup>3</sup> ]	Water [kg/m <sup>3</sup> ]	Density [kg/m <sup>3</sup> ]
CS00	1320,2	-	-	580,9	1890
CS27	829,0	92,1	-	405,3	1280
CS41	952,5	-	105,8	465,6	1530



## Cement pastes dosages by volume

Pastes	Cement [m <sup>3</sup> /m <sup>3</sup> ]	HGMS27 [m <sup>3</sup> /m <sup>3</sup> ]	HGMS41 [m <sup>3</sup> /m <sup>3</sup> ]	Water [m <sup>3</sup> /m <sup>3</sup> ]
CS00	0,42	-	-	0,58
CS27	0,26	0,33	-	0,41
CS41	0,30	-	0,23	0,47



# Cement carbonation under CCS conditions



## Carbonation conditions in the lab

pH > 9



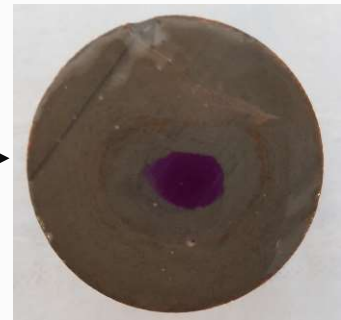
Properties before  
carbonation



[scCO<sub>2</sub>] 100% H.R.  
90°C - 20 MPa – 60 days

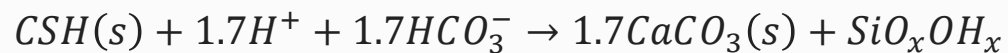
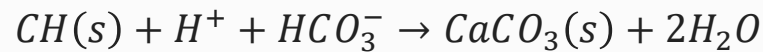
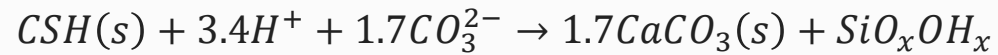
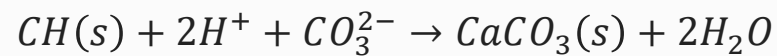
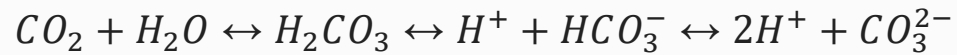
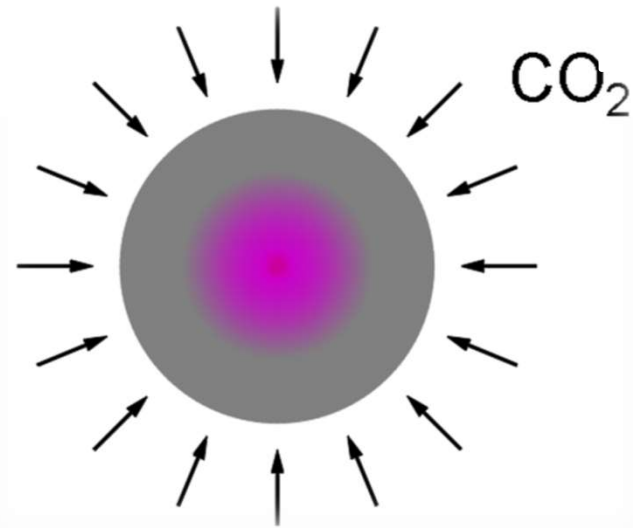
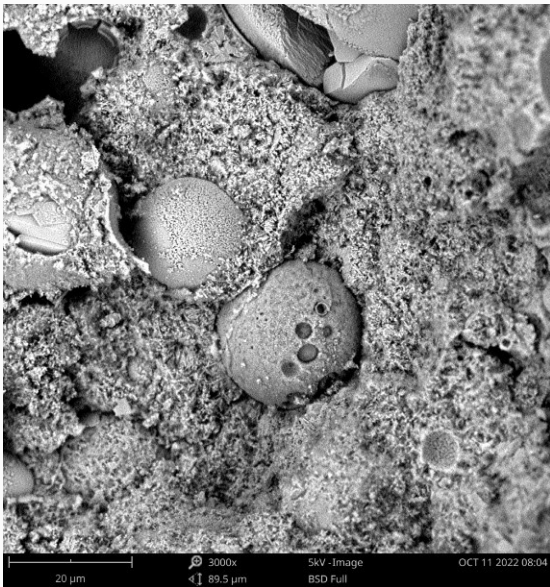


pH < 9



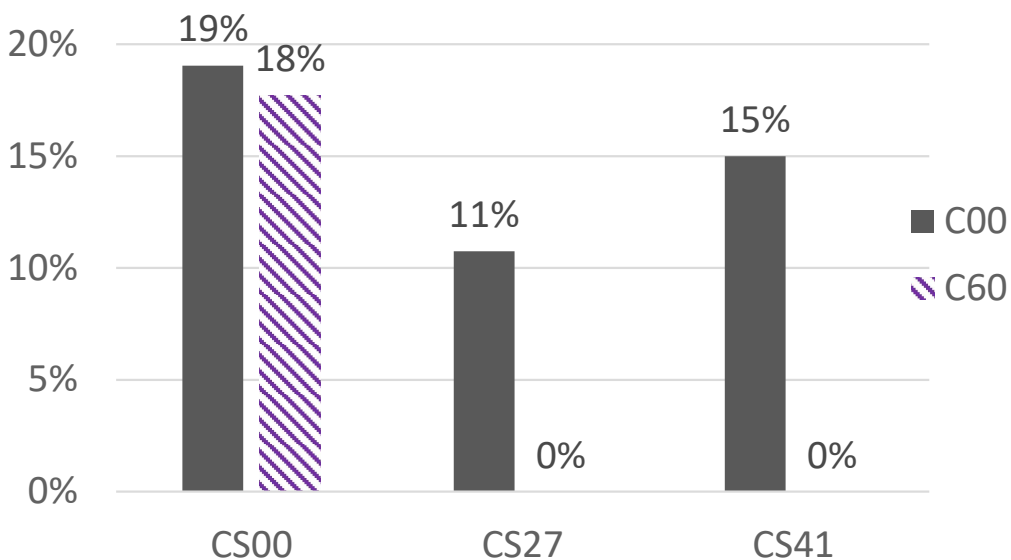
Properties after  
carbonation

## Cement paste carbonation

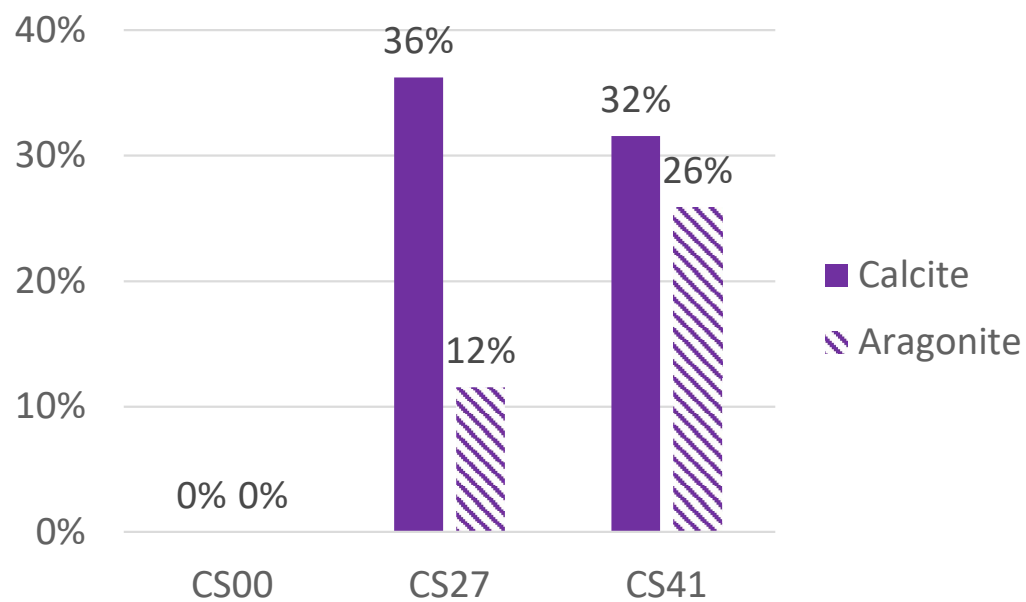


## CH and CaCO<sub>3</sub> content – XRD & Rietveld

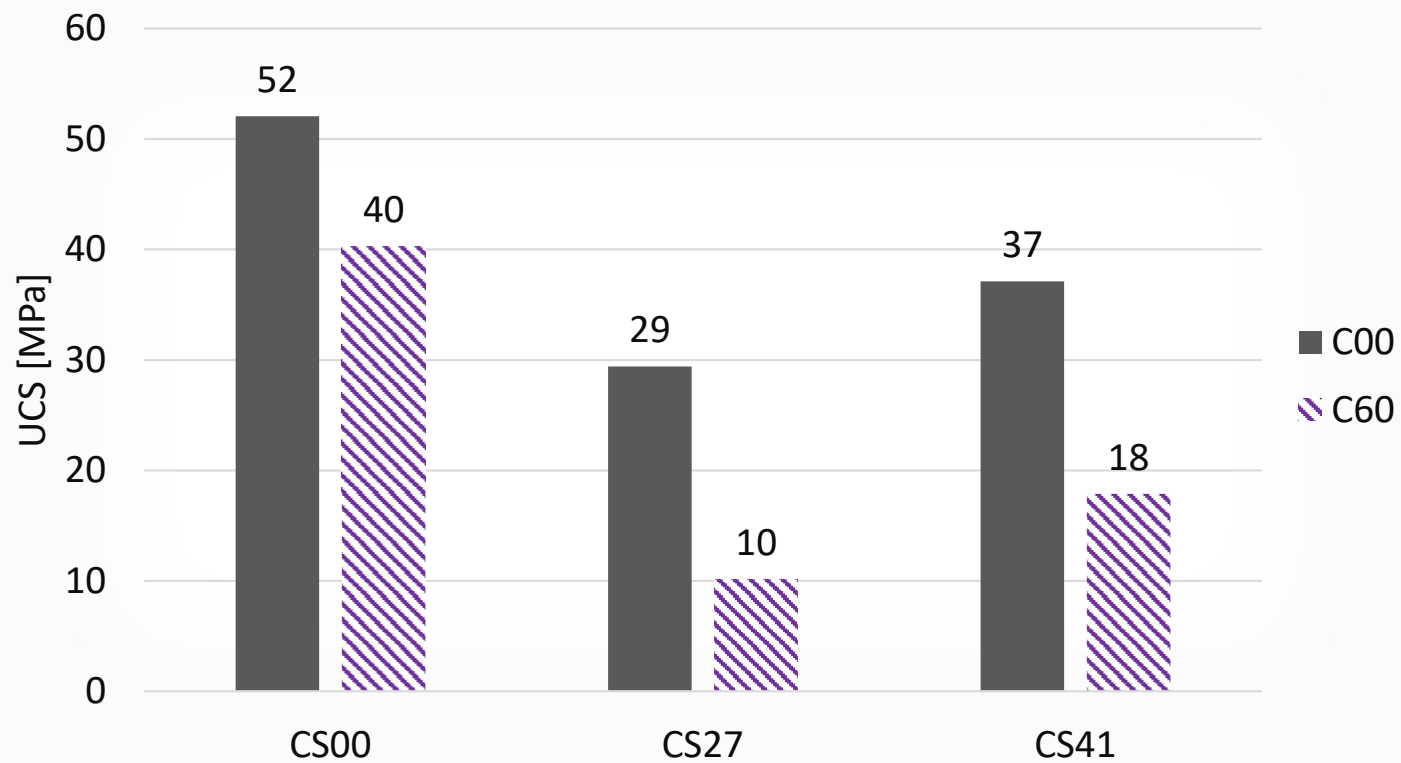
CH content



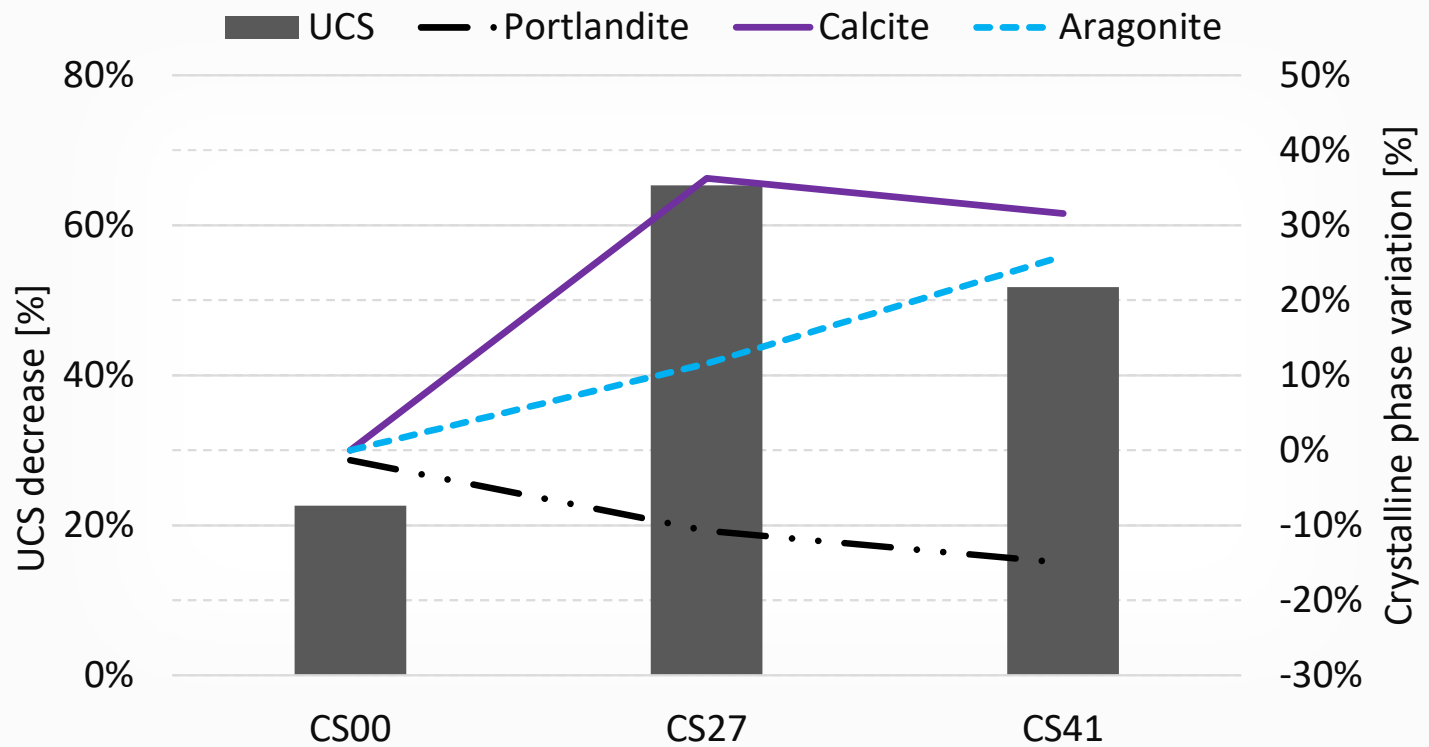
CaCO<sub>3</sub> content (after carbonation)



## Uniaxial compressive strength (UCS)



## XRD and UCS results comparison



## Conclusions

- Preliminary results on the influence of HGMS lightened cement paste under CO<sub>2</sub> geological storage conditions.
- Complete CH consumption for CS27 and CS41, while almost no change in CH content found for CS00. High increase in CaCO<sub>3</sub> polymorphs in CS27 and CS41.
- UCS is degraded after the supercritical carbonation process. Regarding the fraction of the initial strength, the most affected cement paste is CS27.
- Some correlation between CH consumption and calcite formation and UCS results was obtained.



Thank you very much!